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COMPOSITION AND STRUCTURE OF SOL – GEL PLATINUM-DOPED SILICATE FILMS

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X-ray electron spectroscopy and atomic force microscopy are used to investigate silicate films obtained by the sol–gel method and doped with 1, 10, and 20% platinum. The changes in the structure of a silicate film, which are due to doping with platinum, and the effect of the platinum concentration and heat-treatment temperature and atmosphere on the composition and surface morphology of the doped films are determined.

Platinum-doped silicate films are employed as catalytic coatings in thin-film gas sensors used for H_2, NO_x, CO, CH_4, and C_3H_8 analysis [1]. The basic requirements imposed on these films are mechanical strength, determined by the charge state, and a uniform platinum distribution platinum over the film thickness.

Our objective in the present work is to investigate the changes occurring in the structure of a silicate film as a result of doping with platinum and the effect of the platinum concentration and heat-treatment temperature and atmosphere on the composition and surface morphology of the doped films.

Silicate films with the composition $(100 - x)SiO_2 \cdot xPtO_2$ ($x = 0$, 1, 10, and 20%[2]), obtained by the sol–gel method from tetraethoxysilane with platinum chloride added, were investigated. After deposition on a polished single-crystal silicon substrate, the films were heat-treated in a nitrogen or oxygen atmosphere at 450 and 500°C for 15 min.

The surface morphology of the films was investigated by atomic force microscopy (AFM) using a Solver P-47 scanning probe microscope in the semicontact regime in air and silicon probes manufactured by the NT MDT Company.

An x-ray electron analysis of the composition and chemical structure of the films was performed with a ÉS-2401 spectrometer. The spectra were excited by MgK_α radiation. The surface of the samples was cleaned and the samples were etched layer-by-layer by bombarding them with 1 keV argon ions. A method based on the Fourier transform with an improved convergence was used for the mathematical analysis of the spectra [2].

X-ray photoelectron spectroscopy (XPES) has been used now for several decades for analyzing the composition and chemical state of elements. Analysis of the accumulated experimental data has revealed a correlation between the bond energy of the O1*s* line and the oxygen – element interatomic distance in oxides and oxygen-containing salts [3]. A change of 0.03 nm in the distance corresponds to a shift of the O1*s* line by approximately 1.0 eV. A change of the Si – O – Si angle by 10° results in a shift of the Si2*p* line by approximately 0.3 eV [4]. In our previous work we investigated the standard reference spectra of glassy and crystalline quartz and showed that the bond energies E_{bd} O1*s* = 533.1 eV and Si2*p* = 103.4 eV are characteristic for 5,6-member ($Q_{5,6}$) silicon-oxygen structures (rings) and E_{bd} O1*s* = 532.1 eV and E_{bd} Si2*p* = 102.2 eV for 3,4-member rings ($Q_{3,4}$) [5]. On the basis of these results, in the present work we determined the content of the structural components in silicate films obtained by the sol – gel method.

An AFM image of the surface of single-crystal polished quartz used as a substrate for silicate films with surface protrusions not exceeding 1 nm is displayed in Fig. 1*a*.

Effect of platinum on the structure of silicate films. An undoped silicate film [6] and a film doped with platinum (10% PtO_2) were investigated. Both films were heat-treated in a nitrogen atmosphere at 450°C.

An undoped silicate film has a porous structure with 30 – 100 nm pores (Fig. 1*b*). The total surface area of the pores is approximately 30% of the total surface area of the film. The characteristics of the x-ray electronic O1*s* and Si2*p* spectra of the films obtained by the sol – gel method and heat-treated in a nitrogen atmosphere at 450°C are presented in Table 1. The investigations showed that, aside from silicon and oxygen, carbon (6%) and nitrogen (no more than 1%) are present in the film.

Analysis of the Si2*p* an O1*s* spectra of an undoped silicate film (Table 2) shows that, compared with bulk silicate

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[2] Here and below, the weight content unless otherwise stated.

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TABLE 1.

Sample	Position of the spectral components (E_{bd}, eV)			
	O1*s*		Si2*p*	
	spectrum, eV	atomic content of the elements, %	spectrum, eV	atomic content of the elements, %
SiO_2	531.1	6.2	102.2	17
	532.1	50.0	103.4	63
	533.1	40.0	104.6	20
	534.2	3.8		
SiO_2 + 10 % PtO_2	531.4	14.0	102.4	10
	532.3	66.0	103.2	54
	533.3	20.0	104.2	36
SiO_2 + 20 % PtO_2	531.8	7.0	102.4	32
	532.4	34.0	103.4	52
	533.2	59.0	104.3	16

TABLE 2.

Sample	Heat-treatment atmosphere	Content of structural units, %			
		$Q_{3.4}$	$Q_{5.6}$	R – Si – O	H – (SiO_4)
SiO_2 (glass)	Air	25	75	–	–
SiO_2 (film)	Nitrogen	40	50	10	–
SiO_2 + Pt (film)	″	10	10	50	30
SiO_2 + Pt (film)	Oxygen	20	20	40	20

glass obtained by vacuum remelting, the ratio of few- and many-member structures in the films is shifted toward a high content of few-member structures.

The surface morphology of the film doped with platinum is presented in Fig. 2. Uniformly distributed 500 × 500 nm formations with a smaller substructure can be seen on the surface. Investigation of the surface of the film in the phase-contrast regime shows that the structural-phase composition of these formations is different from that of the matrix of the film. The strength of the doped film is lower that that of the undoped film — after the same section of the doped film is scanned three or four times the topography of the surface being studied changes.

The x-ray electron studies established that, besides silicon and oxygen, carbon and nitrogen are also present in the doped film. In addition, the atomic content of carbon is much higher than in the undoped film (6 and 15 – 30%, respectively). The carbon is bound in hydrocarbons (E_{bd} C1*s* = 285.0 eV) and organosilicon structures of the type Si – (CH_3) – O (E_{bd} O1*s* = 533.1 eV, E_{bd} Si2*p* = 102.2 eV, E_{bd} C1*s* = 284.8 eV) [7], and it is also present as graphitic carbon (E_{bd} C1*s* = 283.6 – 284.0 eV) [8]. The silicon is bound in silicon – oxygen structures (few- and many-member structures) and silicon nitride (E_{bd} Si2*p* = 102.2 eV). Sili-

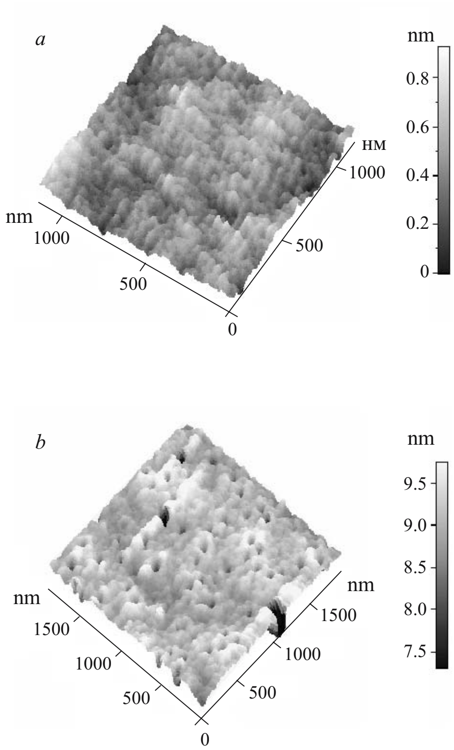


Fig. 1. Surface topography of a silicon single crystal used as a substrate for silicate films (*a*) and of an undoped silicate film heat-treated in a nitrogen atmosphere at 450°C (*b*).

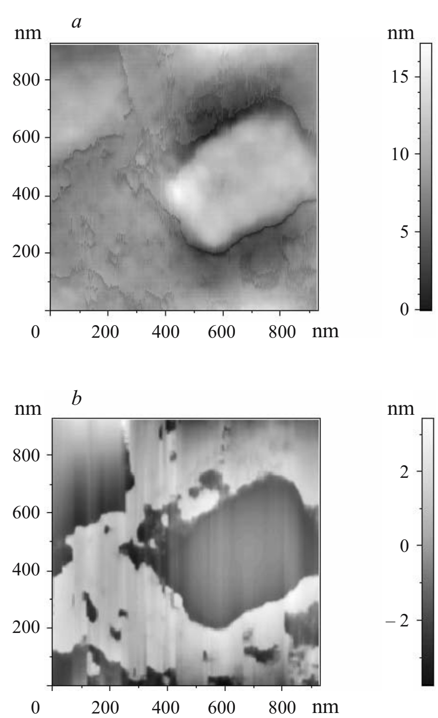


Fig. 2. Surface topography of a silicate film doped with platinum (10% PtO) and heat-treated in a nitrogen atmosphere at 450°C: topographic (*a*) and phase-contrast (*b*) images of a formation on the surface of the film.

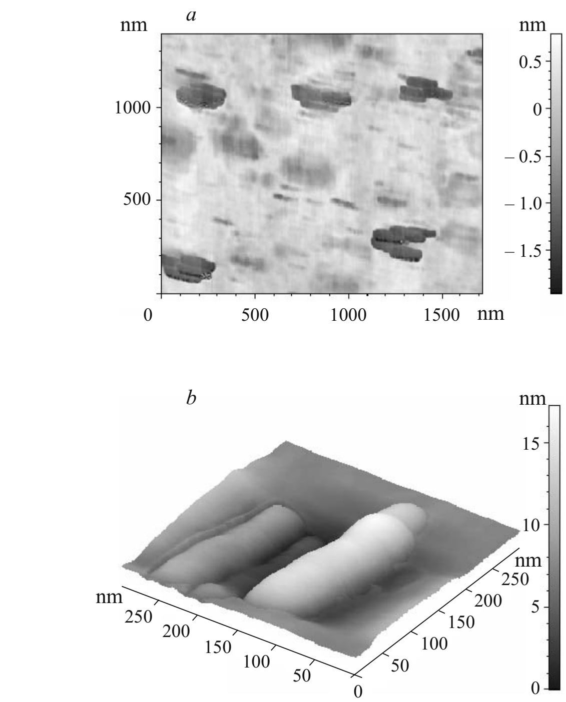


Fig. 3. Surface topography of a platinum-doped (10% PtO) silicate film heat-treated in an oxygen atmosphere at 450°C: phase-contrast (*a*) and formation-topographic (*b*) images of the surface.

con atoms with E_{bd} Si2*p* = 104.6 eV and oxygen atoms with E_{bd} O1*s* = 534.2 eV are bound in compounds of the type H_2SiO_3 [3].

The ratio of few- and many-member organosilicon structures, just as in the undoped film, is shifted toward a higher content of few-member structures. Approximately 20 – 24% of the total carbon content in the film is the form of free (graphitic) carbon. About 80% of the total carbon is bound in organic radicals. Organic radicals in the structure of the films weaken the films. This is manifested as damage done to the film surface by the microscope probe.

Effect of the heat-treatment temperature and atmosphere on the composition of doped silicate films. Films doped with platinum (10% PtO_2) and heat-treated at 450 and 500°C in nitrogen and oxygen atmospheres were studied.

At 450°C the heat-treatment atmosphere affects the size and shape of the formations on the film surface. In contrast to the film heat-treated in a nitrogen atmosphere (see Fig. 2), 150 × 50 nm formations merged into four- and five-particle aggregates form on the surface of the film heat-treated in an oxygen atmosphere (Fig. 3).

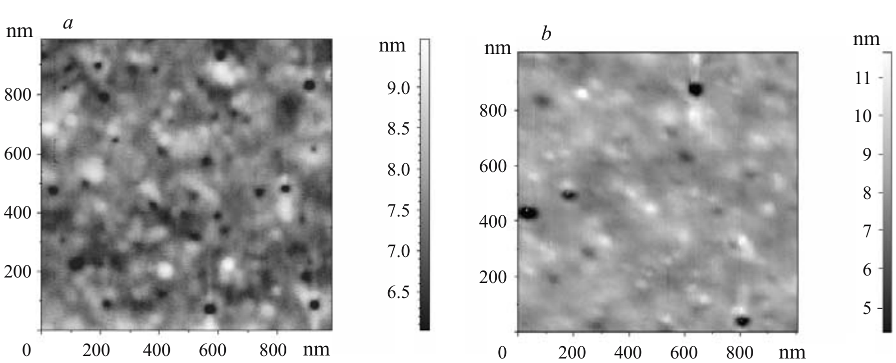
In contrast to films heat-treated at 450°C, the medium has no appreciable effect on the surface morphology of the films heat-treated at 500°C. Hemispherical 50 – 100 nm formations consisting of a different phase are uniformly distributed on the surface of the films heat-treated in nitrogen and oxygen atmospheres (Fig. 4) [9].

The heat-treatment temperature affects the charge state of the platinum: at 450°C the platinum in the film is the form Pt_3O_4 and Pt^0 while at 500°C only the singly charged state Pt^0 is observed. Thermodynamic analysis confirms this dependence of the charge state of platinum on the heat-treatment temperature.

A change in temperature does not affect the content or the concentration profile of the carbon distribution in the films heat-treated in nitrogen and oxygen atmospheres (Fig. 5). The carbon concentration on the surface of films heat-treated in oxygen at 500°C is approximately two times higher than the surface of films heat-treated at 450°C. As the distance from the surface of the films heat-treated at 450°C increases, the carbon content decreases and, conversely, it increases in films heat-treated at 500°C. Increasing the heat-treatment temperature approximately doubles the carbon concentration in the films.

Effect of the platinum content on the composition of silicate films. Films doped with platinum (1, 10, and 20% PtO_2) and heat-treated in nitrogen and oxygen atmospheres at 500°C were studied.

As the platinum content in the films increases, the number of formations on their surfaces increases. The distribution of the formations on the surfaces of films with 1 and 10% PtO_2 is uniform, and for 20% PtO_2 the formations coalesce into agglomerates whose distribution is non-



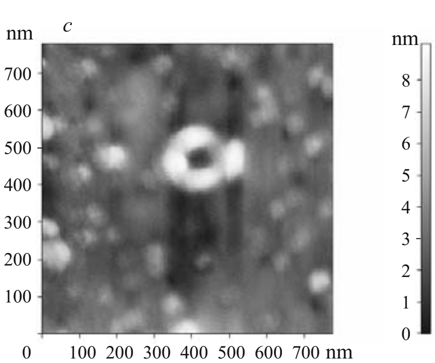


Fig. 4. Surface topography of platinum-doped silicate films heat-treated in a nitrogen atmosphere at 500°C: *a*, *b*, and *c*) 1, 10, and 20% PtO_2, respectively.

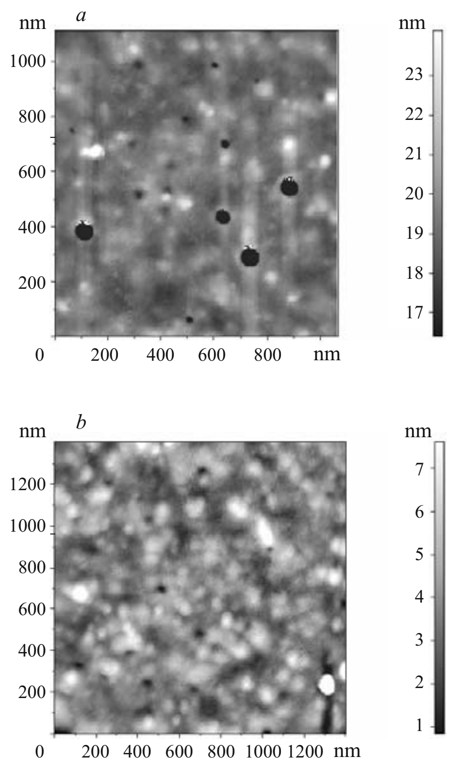


Fig. 5. Concentration profiles of the distribution of the elements over the thickness of a surface layer of silicate films doped with 10% PtO_2 and heat-treated in nitrogen (*a*) and oxygen (*b*) at 450 and 500°C.

uniform. In addition, the porosity of the films decreases as the platinum content increases.

The content and character of the carbon distribution over film thickness is observed to depend on the platinum concentration. In films with 1% PtO_2 the carbon concentration decreases inward from the surface, whereas it increases in films with 10 and 20% PtO_2. In addition, this dependence is sharper in films which are heat-treated in oxygen — in films with 1 and 20% PtO_2 the carbon concentrations on the surface and in the interior volume of the films differ by a factor of 3. This difference is much smaller in films heat-treated in a nitrogen atmosphere.

In summary, the content of few-member silicon – oxygen structures is higher in undoped silicate films obtained by the sol – gel method than in bulk silicate glass.

Introducing platinum into sol increases the carbon content in the films. The carbon is present in the form of graphitic carbon and organic radicals. The organic radicals, which become incorporated into the film structure, weaken the structure of the films. This is seen as damage done to the film surface of the films by the microscope probe.

The platinum concentration in silicate films affects the carbon content and the distribution of carbon and platinum over thickness and the surface morphology (pore size and the dimensions and number of the formations).

The heat-treatment temperature affects the surface morphology, the amount of carbon in the films, and the carbon and platinum distributions over film thickness.

In the case of heat-treatment at 450°C the atmosphere affects the morphology and strength of the films. No such effect was observed at 500°C.

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